Chemistry—50 Years of Exploring the Material World

Of the 70 or so people who came to work at the Livermore branch of the University of California Radiation Laboratory in September 1952, nearly a third were chemists, chemical engineers, and material scientists, hired to support the Laboratory's fledgling nuclear weapons program. These personnel had two immediate tasks. At the front end of a weapon's development, Livermore chemists had to be able to form parts out of unusual materials such as plutonium and uranium for nuclear test devices. Then after each device was tested, they had to be able to analyze the radioactive components of the leftover debris and gases to help determine the weapon's performance.

Livermore's chemists wasted no time setting up a processing laboratory in the only available room equipped with running water: the women's restroom of the bachelor officers' quarters of the former naval air station that was the home of the new "Rad Lab." By spring 1953, they had also put a laboratory in the former dispensary and set up a chemical fabrication capability in the assembly hall. The women's restroom and the assembly hall were merely temporary measures. The first permanent building at the Livermore site, completed in 1954, was built for the chemistry organization.

As the Laboratory grew and evolved, so did its chemistry organization. From studies of isotopes—particularly in the actinide group of elements—Livermore chemists built a first-class institute to study heavy elements and helped discover new elements. They developed high explosives that were safer but still delivered the power needed by weapons designers, and they tailored other special materials for specific applications. Chemists were the first at the Laboratory to use computers to automate laboratory processes. And their involvement with the computational world didn't stop there. With the explosion in computational abilities and sophisticated experimental capabilities of the past decade, chemists and material scientists are gaining a more complete and fundamental understanding of the behavior of materials as esoteric as aging plutonium and as common as the surface of water.

> *Nothing in life is to be feared. It is only to be understood.*
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> *—Marie Curie, physicist and winner of the Nobel Prize for physics (1903) and chemistry (1911)*

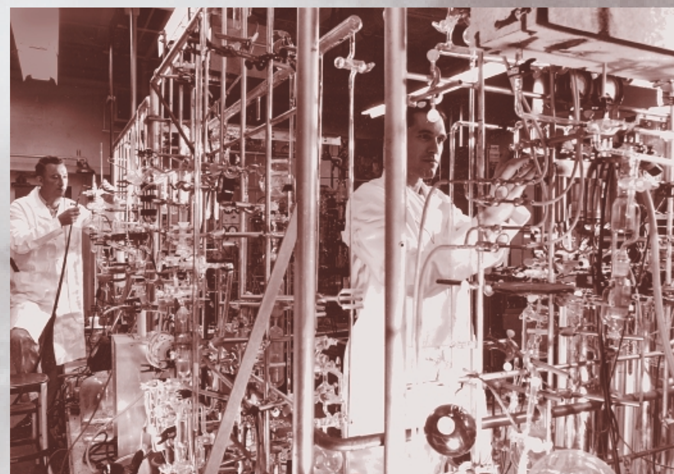
Of Yields, Isotopes, and Heavy Elements

In his preliminary plan for the Laboratory, Herb York, the young physicist whom Ernest O. Lawrence designated to get the Livermore project up and running, made specific note of the need for a radiochemistry group. Radiochemistry, a fairly new field in 1952, is the study of radioactive substances and is closely tied to nuclear chemistry, which is the study of the atomic nucleus, including fission and fusion reactions and their products. Radiochemical diagnostics were crucial to determining how well a device performed in a test. An exploding device produces large neutron fluxes. Those neutrons interact with the device materials, creating different isotopes and other elements. By determining the differences between the materials in the weapon before the explosion and those produced by the explosion, scientists can deduce what happened during the test.

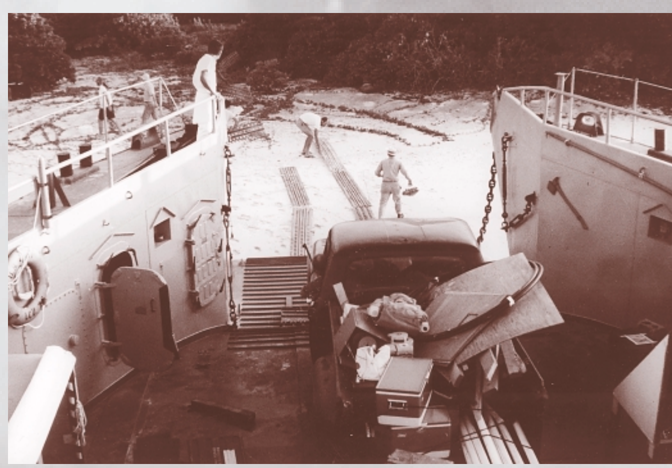
Obtaining those results was a long, extremely complex process, and not without its hazards. (See the box on p. 27.) Livermore conducted nuclear experiments for nearly four decades, at first in the atmosphere and later underground. Throughout that time, radiochemists examined fission products, heavy elements, products resulting from neutron capture, products from other neutron interactions, and short-lived gases. Their results—when combined with results from nonchemical diagnostics (such as those described in *S&TR*, April 2002, pp. 22–24)—gave weapon designers a picture of how well the device worked.

For example, to determine the fusion yield of a device, chemists would add detectors—small quantities of specific elements, such as yttrium—to various parts of a device as it was being made. Radiochemist David Nethaway, who started his Laboratory career during the early days of atmospheric testing, explains, "Certain reactions between neutrons and detector materials such as yttrium only occur when the neutron energies are above a particular threshold." For instance, the reaction that converts an atom of yttrium-89 to an atom of yttrium-88 plus two neutrons only occurs when a neutron with an energy greater than 12 megaelectronvolts (MeV) smashes into the yttrium-89 atom. "By measuring the amount of yttrium-88 in debris samples recovered from the test, we could determine the fluence of 14-MeV neutrons, and from that we infer a fusion yield," says Nethaway. (See *S&TR*, May 2002, pp. 16–21.)

Over time, Livermore's radiochemical expertise was applied to other projects as well. In the early 1970s, radiochemists performed radiological surveys of Enewetak Atoll in the Pacific Ocean to prepare for the islanders' return after the atmospheric tests of the 1950s. The initial focus was on elements of particular use to nuclear weapons research and testing, including the set of elements known as actinides. This work led to the establishment of the University of California's Glenn T. Seaborg Institute for Transactinium Science at Livermore in 1991. Since the Laboratory's early days, Livermore chemists have also been involved in searches for new elements to add to the periodic table. This work includes detailed studies of debris from the Hutch Event, a 1969 underground test specifically designed to produce superheavy



A 1957 photo of Livermore's chemists setting up equipment in a gas analysis laboratory. Rare gases such as krypton and xenon were regularly analyzed as part of the chemical diagnostics for nuclear weapon tests.



In the mid-1950s, inhabitants of Enewetak Atoll in the South Pacific relocated when the U.S. began conducting atmospheric nuclear tests nearby. When the islanders were preparing to reinhabit Enewetak, Livermore led a research force, members of which are pictured here, drawn from 19 federal and scientific organizations to perform a radiological survey of the soils, plants, and marine environment of the islands.

elements, and culminates with the recent synthesis of elements 114 and 116. (See *S&TR*, January/February 2002, pp. 16–23.)

After a decade of underground testing at the Nevada Test Site, Livermore's radiochemists began studying the movement in groundwater of radioactive elements from those tests. Using both radioactive and stable isotope tracers, these scientists investigated groundwater sources, ages, travel times, and flow paths. Having proved their usefulness at the Nevada Test Site, isotope tracer methodologies have since been applied to other water resource projects, including one for the Orange County Water District in southern California. (See *S&TR*, November 1997, pp. 12–17.)

Today, radiochemists and nuclear chemists are also contributing their skills in radiation detection, gamma-ray spectrometry, and mass spectrometry to programs aimed at preventing nuclear proliferation. For example, sophisticated codes originally developed to analyze the complex gamma-ray emissions from nuclear explosion debris now form the standard for analyzing samples collected by the International Atomic Energy Agency (IAEA) and other international organizations. Nuclear chemists are also developing gamma-ray imaging technology that can be applied to a range of counterterrorism applications.

Developing Safe Explosives, New Polymers, and More

In the division assigned to develop and design thermonuclear weapons and testing devices, York also sketched in spots for chemists and metallurgists, noting, "[C]ertain unusual mixtures of materials are very frequently needed . . . and are normally unobtainable outside." Over the years, Livermore's material specialists have dealt with nearly every element in the periodic table. Sometimes they created new materials, and sometimes they synthesized existing materials in unusual or exotic ways or combinations.

At the start, new materials development was strictly related to nuclear weapons and mostly involved unusual alloys (including a corrosion-resistant "stainless" uranium) and plastics. About those earliest days, chemical engineer Barney Rubin recalled, " A major activity was becoming expert in making plastic parts or fabricating components out of weird exotic materials that used plastics as binding agents. We also got heavily into metallurgy. We weren't material scientists in the sense that they are known now. We were sort of kludging things together as best we could—sometimes by intuition and black art, sometimes by science, and sometimes by a combination of the two."

In the area of high explosives (HE), Livermore started pretty much from scratch. The chemists turned for assistance to the centers for HE expertise —Los Alamos and certain Department of Defense laboratories. Livermore's chemists worked closely with weapon designers to develop an HE program that made sense for the design effort, eventually creating the LX series of explosives for Livermore's weapons.

"We had a general goal of trying to get more bang per unit volume," says Gus Dorough, an early leader of the chemistry organization. "It was a point that clearly interested the nuclear

A collaboration with Lawrence Berkeley researchers resulted in the discovery of element 106 in 1974. A separate collaboration (pictured above) with the Joint Institute for Nuclear Research in Dubna, Russia, that began in 1989 led to the discovery of several new isotopes in the early 1990s and in the recent synthesis of superheavy elements 114 and 116.

Fran Foltz examines crystals of the insensitive high explosive triamino-trinitrobenzene (TATB) under the microscope. The background shows TATB crystals at high magnification.

designers, and it turned out to be a very sophisticated and subtle subject. It's not just a matter of more potential energy per unit volume; it's a matter, for instance, of how that energy is released, what kind of chemical detonation products are formed, and the equations of state of those products. Just developing a good technique to measure energy release so we could screen new compounds was no simple matter."

Several empirical tests for measuring HE energy and sensitivity were developed, including the Susan Test (named after Dorough's daughter), which measured safety properties of explosives under simulated accident conditions. Livermore also developed insensitive HE that met the designers' requirements while significantly improving the safety and survivability of munitions, weapons, and personnel. One such, triamino-trinitrobenzene (TATB), is nearly invulnerable to significant energy release in plane crashes, fires, and explosions or to deliberate attack with a small firearm. (See *S&TR*, November 1996, pp. 21–23.)

Polymers—substances made of giant molecules formed by the union of simple molecules—have long been of interest to the Laboratory. In the 1980s, a low-density lightweight polymer called aerogel, first invented in the 1930s, caught the attention of Livermore chemists who went on to create superlight silica aerogels and organic aerogels for the Strategic Defense Initiative. (See *Energy & Technology Review*, November 1994, pp. 16–17.)

Since then, Livermore has developed and improved aerogels for national security applications and synthesized electrically conductive inorganic aerogels for use as supercapacitors and as a water purifier for extracting harmful contaminants from industrial waste or for desalinating seawater. Recently, chemist Glenn Fox led a desalinating project to bring atomic-level control to the design and synthesis of organic aerogels. (See *S&TR*, June 2000, pp. 23–25.) A team headed by chemist Randy Simpson created aerogellike energetic materials with structures that can

Samples from the Sky—Radiochemistry in the Era of Atmospheric Tests

The atmospheric tests of nuclear weapon devices presented unique challenges in data gathering for radiochemists. Right after an atmospheric test, much of the material—radioactive particulates and gases—resides in the signature mushroom cloud. The objective of researchers was to get representative samples of this cloud for analysis.

In an interview conducted nearly 20 years ago, the late Harry Hicks, one of the early radiochemists at Livermore, described what was involved in collecting and processing the samples. The first step was to look at the expected yield of an upcoming test to estimate the size of the cloud and its altitude. "Then you look at the mix of fission and fusion," said Hicks. "The fission products tell you what the radiation level is in the cloud. What you want to do is to send the aircraft in to get your samples, but you don't want to overexpose the crews."

A plane with a Laboratory chemist would be in the air before shot time. After the shot went off, the chemist would observe the cloud and its formation. "If you saw a wisp of cloud or a likely spot," said Hicks, "you'd go over and find out whether it was radioactive or not by flying through to see if you wanted to sample the thing." If the cloud appeared promising, an Air Force sample plane would fly in and obtain a sample. Particulates were captured on large filter papers mounted in pods on each wingtip. Short-lived gases were drawn through the filter, compressed, and stored in 30-centimeter spheres.

Chemist Harry Hicks ready to board an Air Force RB-57 sampling plane.

Radioactive elements decay constantly, so time was of the essence. Planes landed immediately after obtaining samples, and the samples were removed, packaged, and rushed back to Livermore by courier plane. The samples from Pacific tests normally came in at seven or eight o'clock at night, and the chemical analysis—which took place inside gloveboxes in a building without air-conditioning—began. First, a chemist dissolved the filter papers, a nasty business involving beakers, hot plates, red fuming nitric acid, and hot perchloric acid. Once the papers were dissolved, each desired chemical element had to be completely separated out and completely cleaned of other materials. "Our procedures were relatively new," noted Hicks, "and they weren't exactly reliable, so we would do everything in quadruplicate, hoping we got three, or two, to agree. It just took a long time to be able to say, 'I'm sure that there's nothing but that element there.'"

As the shots got larger, the test clouds got larger and higher, so planes could only sample the tail end of the cloud. In the early 1960s, Livermore researchers had the unique idea of using rockets to determine how representative such samples were. "With remotely controlled rockets, we were able to get samples from higher up and earlier than we could with planes flown by pilots," says retired Livermore chemist John Kury. Results from the rocket tests showed that plane samples—taken later and lower—were indeed representative of the clouds. "At the time, this project made a real difference in our understanding of the radiochemistry needed to analyze device performance," notes Kury, "and it made a real difference for years after, by validating the samples done in earlier tests."

be engineered at the nanometer scale. (See *S&TR*, October 1999, pp. 19–21.)

Aerogels aside, polymers have long been used by Livermore's material scientists to create smooth, spherical thin-walled shells or coatings for targets used in laser fusion experiments. (See *S&TR,* June 1997, pp. 22–24.) Another organic polymer, Mercaptoplex, was originally developed at Livermore for use in processing nuclear fuel rods. Mercaptoplex has found another application in removing toxic mercury from industrial waste streams and public water supplies. (See *S&TR*, November 1999, pp. 17–19.)

A piece of extremely lightweight aerogel poised on soap bubbles. Aerogels have the highest internal surface area per gram of material of any known material and also exhibit the best electrical, thermal, and sound insulation properties of any known solid.

Multilayers—exceedingly thin alternating layers of materials—are another example of the Laboratory taking an existing material, developing it further, and expanding its applications. First demonstrated more than 50 years ago, multilayers offer extraordinary strength, hardness, heat-resistance, and unexpected new properties. In 1987, chemist Troy Barbee led a team that designed and synthesized multilayer optics for the soft x-ray and extreme ultraviolet regions of the spectrum. Telescopes with these multilayer x-ray optics were used to capture high-resolution, wide-field x-ray images of the Sun. (See *S&TR*, December 1997, pp. 12–19, and December 1999, pp. 11–13.) Multilayer optics are also used in electron microprobes, scanning electron microscopes, and particle beamlines in accelerators. Multilayer optics are crucial to the current collaboration among Livermore, other Department of Energy laboratories, and private industry to develop extreme ultraviolet lithography for manufacturing the next generation of microcomputer chips. (See *S&TR*, November 1999, pp. 4–9.)

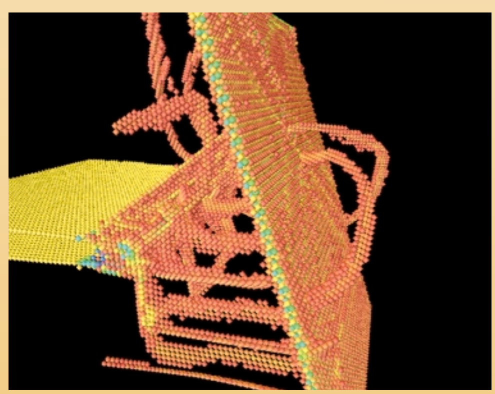
Tools of the Chemistry Trade

The tools of Livermore's chemists and material scientists extend beyond the typical array of glassware and general chemistry apparatus to include nuclear radiation counting instruments, accelerators, vapor deposition equipment, a variety of microscopes and mass spectrometers, and, of course, computers.

Chemists were the first at the Laboratory to integrate computers with laboratory equipment using a PDP-7 in the gas-analysis laboratory in 1965. By 1971, the computer was simultaneously controlling an assortment of experimental equipment including a vacuum-fusion device, a mass spectrometer, an emission spectrograph plate reader, and an automatic sampling atomic absorption system.

As computers evolved, so did the chemistry organization's applications of them. In the mid-1970s, chemistry designed the first completely computerized triple-quadrupole mass spectrometer, a marvel of its time. The system allowed chemists to detect and measure less than 1 nanogram of a sample and was used to analyze trace sulfur compounds in processing oil shale and to investigate the thermal decomposition kinetics of high explosives.

Today, massively parallel computers are a mainstay of efforts to understand material properties and behaviors. For instance, computer simulations of energetic material properties led theoretical chemist Riad Manaa to propose a novel energetic material consisting of a nitrogen analog of the familiar carbon buckyball. (See *S&TR*, June 2001, pp. 22–23.) Chemists are also supporting efforts to model chemical warfare agents by developing kinetic models for surrogate and actual agent chemicals, which could then be used in atmospheric dispersion and other accident and terrorist scenarios. As part of this effort, chemists recently developed the first detailed kinetic model for the agent sarin and modeled comparisons of the chemistry of sarin and its surrogates.



Kinetic model for the agent sarin.

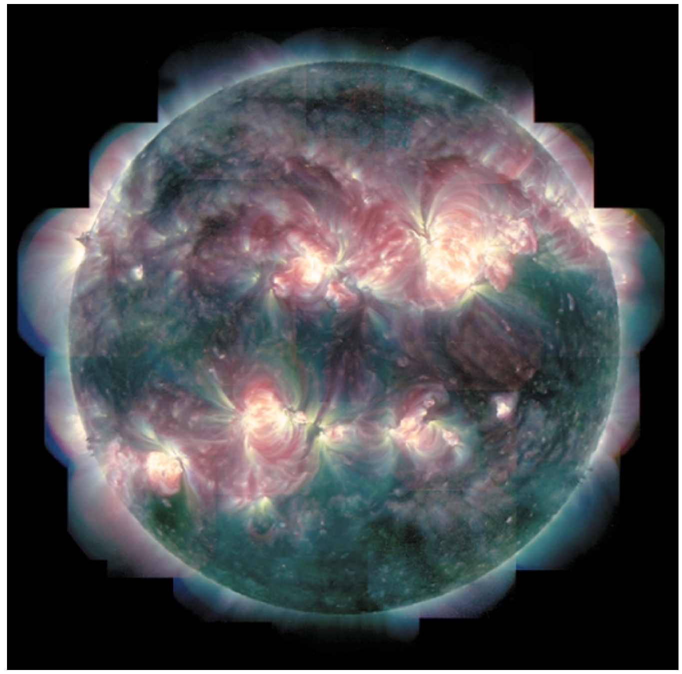
Delving into Material Behavior and Properties

"Exploratory, basic scientific research is key to the Laboratory's success in fulfilling its missions," explains Hal Graboske, associate director for Chemistry and Materials Science (C&MS). "In all of our work, we are pushing the frontiers of science and often must know the basics before we can proceed with the more complex." To meet the Laboratory's programmatic needs, Livermore's chemists and material specialists have often returned to the basics, investigating the behaviors and properties of elements and various materials in ever-increasing detail and at more encompassing scales.

Nuclear weapons include highly reactive metals—plutonium and uranium—as well as organic compounds that degrade over time from exposure to radiation, high temperatures, and accumulated gases. In the past, scientists at Livermore studied how various materials aged and interacted under stockpile conditions to guide the selection and use of the best available materials for new weapons. They developed accelerated aging tests, subjecting small samples of candidate materials to elevated temperatures for a day to several months. These tests measured gas evolution, weight loss, and chemical reactions with contacting materials. Materials that passed this screening were assembled into configurations that modeled the material interfaces in the weapon design and tested at temperatures appropriate to service conditions for months or even years.

With the advent of stockpile stewardship in the 1990s, material scientists looked for ways of predicting the lifetime of key weapon materials and developing "age-aware" material models for use in codes that predict the lifetime of the overall weapon system. (See *S&TR*, September 1999, pp. 4–11.) For example, metallurgist Adam Schwartz is part of a team conducting experiments to measure the structural, electrical, and chemical properties of plutonium and its alloys and determine how these materials change over time. (See *S&TR*, March 2001, pp. 23–25.) "Plutonium is a complex and perplexing element," notes Schwartz. "For instance, it has seven temperature-dependent solid phases—more than any other element in the periodic table. Each phase has a different density and volume and its own characteristics." Instruments such as the transmission electron microscope image the microstructure, allowing researchers like Schwartz to see not just the surface, but the internal structure of the material at the atomic scale, providing the measurements needed for Livermore's material models.

It's not just exotic materials such as plutonium that get the close scrutiny. Water, for instance, was the subject of a recent collaboration between Lawrence Livermore and Lawrence Berkeley chemists. (See *S&TR*, November 2001, pp. 20–23.) Any system involving liquid water—hemoglobin in blood, proteins in water—is affected by the way that hydrogen bonds to the oxygen atoms. The researchers developed a technique using synchrotron radiation to determine for the first time the distance of bonds between hydrogen atoms and oxygen atoms at the surface of liquid water.



The Sun's corona seen with x-ray optics designed at Livermore.

The properties and behaviors of materials are also greatly affected by the processes they undergo—whether the process is welding metals or growing crystals. Livermore metallurgist John Elmer has researched details of the welding process since the early 1990s. Dependable welds are important for maintaining the performance and safety of nuclear weapons and play a key role in the long-term storage of nuclear wastes. Recent experiments using x-ray synchrotron radiation have revealed second-by-second changes in a metal's microstructure during welding, providing the first real-time look at the welding process. (See *S&TR*, November 2001, pp. 4–11.)

In the mid-1980s, C&MS researchers began to investigate ways to rapidly grow the crystals used for optical switching and frequency conversion on high-power laser systems. (See *Energy & Technology Review*, November 1994, pp. 3–5.) With the advent of the powerful atomic force microscope in the 1990s, Livermore researchers began to clarify on the nanometer scale the growth mechanisms and three-dimensional structures of widely different solution-based crystals. (See *S&TR*, November 1996, pp. 12–20.)

In the past, advances in materials were accomplished by extensive laboratory testing combined with a healthy dose of guesswork, a time-consuming and often costly approach. As experimental tools such as microscopes have become increasingly powerful, so have the computers used to model and predict material behavior. At Lawrence Livermore, home to some of the most powerful massively parallel computers in existence, C&MS researchers are linking computer simulations to laboratory experiments. (See the box on p. 28.) Codes are now so sophisticated that Livermore researchers are beginning to predict what scientists will see when imaging materials through electron microscopes.

Chemistry's Future Grows with the Laboratory

It's been a long journey for Livermore's chemistry organization from the women's restroom in the old barracks to today's highly sophisticated state-of-the-art laboratories and equipment, from analyzing radiochemical diagnostics for weapon tests to simulating the behavior of materials at the atomic level using supercomputers.

"For the past half-century, our goals have been to provide the right people for the Laboratory's programs and a research environment that fosters growth," says Graboske. "The people have always risen to the challenge, meeting the changing needs and seizing emerging opportunities over the decades." From continued support of the weapons program to dealing with the nation's recent threat of terrorism, the Laboratory's chemistry and materials science experts remain at the cutting edge of scientific discovery.

—Ann Parker

Key Words: actinides, aerogels, atmospheric tests, chemistry, computer simulation, crystal growth, high explosives, isotopes, materials aging, material science, metallurgy, multilayers, multiscale modeling, plutonium, polymers, radiochemistry, radiochemical sampling, welding.
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For more information about the Chemistry and Materials Science Directorate:
www-cms.llnl.gov/

For more about the history of the chemistry organization at Livermore:
www-cms.llnl.gov/50_year_anniversary/

For further information about the Laboratory's 50th anniversary celebrations:
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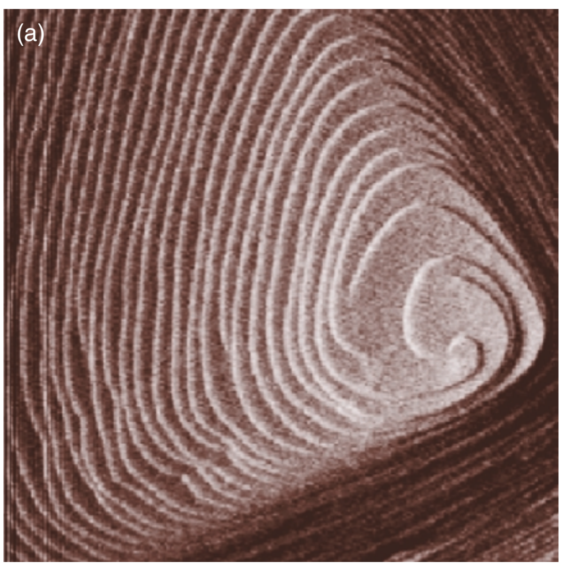

(a) An 8- by 8-micrometer scanned image of the face of a potassium dihydrogen phosphate (KDP) crystal. The morphology and dynamics of crystal growth are relevant to the National Ignition Facility (NIF) as well as to projects that study biomaterials. (b) An example of a large KDP crystal grown for the NIF laser.